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Helium (I) ultraviolet photoelectron spectra (UPS) are reported for the compounds $CR(N^iPr_2)_3$, $Cr(NEt_2)_4$, $Mo(NME_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. The interpretation of the UPS of the paramagnetic dialkylamide, $Cr(N^iPr_2)_3$, was aided by a SGF X_α scattered wave (X_α-SW) calculation on the model ⟶

compound $Cr(NH_2)_3$. In contrast to previous UPS work on $Cr[N(SiMe_3)_2]_3$, ionizations are detectable from the metal MO's of $Cr(N^1Pr_2)_3$. The UPS of the tetracoordinate molybdenum compounds, $Mo(NR_2)_4$, R=Me, Et are in excellent agreement with X-ray crystallographic data on $Mo(NMe_2)_4$ and exhibit a low energy ionization ($\sim$5.3 eV) which is attributable to electron ejection from the essentially pure Mo $4d_{(x^2-y^2)}$ MO of $b_{(1)}$ symmetry. The pentacoordinate compounds, $M(NMe_2)_5$, M=Nb, Ta exhibit very similar UPS and therefore appear to be isostructural in the vapor phase.

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A UV PHOTOELECTRON SPECTROSCOPIC INVESTIGATION OF THE BONDING IN SOME TRI-, TETRA-, AND PENTACOORDINATED DIALKYLAMINO COMPOUNDS OF CHROMIUM, MOLYBDENUM, NIOBIUM, AND TANTALUM.

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(10)

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Abstract: Helium (I) ultraviolet photoelectron spectra (UPS) are reported for the compounds $Cr(N^iPr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. The interpretation of the UPS of the paramagnetic dialkylamide, $Cr(N^iPr_2)_3$, was aided by a SCF X_α scattered wave (X_α SW) calculation on the model compound $Cr(NH_2)_3$. In contrast to previous UPS work on $Cr[N(SiMe_3)_2]_3$, ionizations are detectable from the metal MO's of $Cr(N^iPr_2)_3$. The UPS of the tetracoordinate molybdenum compounds, $Mo(NR_2)_4$, R = Me, Et are in excellent agreement with X-ray crystallographic data on $Mo(NMe_2)_4$ and exhibit a low energy ionization ($\sim$5.3 eV) which is attributable to electron ejection from the essentially pure $Mo\ 4d_{x^2-y^2}$ MO of b_1 symmetry. The pentacoordinate compounds,

$M(NMe_2)_5$, M = Nb, Ta exhibit very similar UPS and therefore appear to be isostructural in the vapor phase.

INTRODUCTION

The use of dialkylamido and disilylamido ligands has permitted the isolation of mono- and dinuclear transition metal derivatives with widely varying coordination numbers.[2] Compounds of this type are well suited to investigation by ultraviolet photoelectron spectroscopy (UPS) because, as shown in previous studies[3-5], the peaks at lower binding energies corresponding to electron ejection from metal-centered MO's, nitrogen lone pair MO's, and metal-nitrogen σ-bonding MO's fall into distinct regions. The UPS data can be used, therefore, not only for the delineation of bonding schemes but also for gaining insights into the stereochemistry of metal amides.

The present paper is concerned with the measurement and interpretation of the UPS of $Cr(N^1Pr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$ and $Ta(NMe_2)_5$. Our interest in the tricoordinate species, $Cr(N^1Pr_2)_3$, was generated by the fact that in the corresponding silylamide, $Cr[N(SiMe_3)_2]_3$, it was impossible to detect UPS peaks corresponding to the ionization of metal-localized MO's.[5] The tetracoordinate dialkylamides, $Cr(NEt_2)_4$ and $Mo(NR_2)_4$, R = Me, Et, are the first Group VI A amides to be studied by UPS; particular interest is associated with these compounds because the molybdenum amides are diamagnetic yet $Cr(NEt_2)_4$ is paramagnetic. Finally, the pentacoordinate amides, $M(NMe_2)_5$, M = Nb, Ta, were investigated because of the apparently close energies of the trigonal bipyramidal and square pyramidal MN_5 geometries and the possibility

of detecting conformational effects in the vapor phase.

A SCF X_α scattered-wave calculation[6] (hereafter referred to as X_α SW) has been performed on the model amide $Cr(NH_2)_3$ to facilitate the interpretation of the UPS data. As is well known, this theoretical approach has the advantage of avoiding the use of Koopmans' theorem[7] by means of the transition state method[8].

EXPERIMENTAL SECTION

Materials. The compounds $Cr(N^iPr_2)_3$[9], $Cr(NEt_2)_4$[10], $Mo(NMe_2)_4$[11], $Mo(NEt_2)_4$[11], $Nb(NMe_2)_5$[12], and $Ta(NMe_2)_5$[13] were prepared and purified as described in the literature.

Spectroscopic Measurements. All UPS data were recorded on a Perkin-Elmer Model PS-18 Photoelectron Spectrometer using a He(I) photon source (21.22 eV). The heated inlet probe was used for all samples and temperatures in the range 35-100°C were necessary to obtain suitable spectra. Each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) used as internal standards. Spectral resolution was maintained between 25 and 50 meV for the argon line. All ionization energies are read as the band maxima, unless otherwise noted, and are the average of at least three different runs.

Computational Procedures. The X_α SW calculation on $Cr(NH_2)_3$ was made by employing the spin-restricted procedure of Johnson and Slater[6], setting the occupation numbers of the 6e and $4a_1$ levels at two and one, respectively, in accord with the

4

observed ground state electronic configuration.[9] The bond dis-
tances and angles for $Cr(NH_2)_3$ were based on those observed
by X-ray crystallography for $Cr(N^iPr_2)_3$,[14] except the N-H
bond distance was taken to be 1.01 Å. The atomic sphere radii
were chosen on the basis of optimizing the virial ratio, and
the outer sphere was set tangential to the hydrogen spheres.[15]
Schwartz's exchange parameters, α_{HF}, were used for chromium
and nitrogen, while Slater's value for hydrogen was used.[16]
α_{OUTER} was taken equal to α_H, while the intersphere exchange
parameter, α_{INT}, was calculated to be 0.7490 on the basis of
averaging the atomic α values according to the numbers of
valence electrons. Spherical harmonics through $\ell = 2$ were
employed for the chromium and outer spheres, while functions
through $\ell=1$ and $\ell=0$ were employed for the nitrogen and hydrogen
spheres, respectively. All SCF calculations were converged
to better than 0.01 eV for each level, maintaining all cores
fixed. The first four IE's for $Cr(NH_2)_3$ were computed by the
transition state method[8].

RESULTS AND DISCUSSION

The tricoordinate compounds, $M[N(SiMe_3)_2]_3$, M=Ti, Cr,
Fe, and $Cr(N^iPr_2)_3$ represent examples of the stabilization of
low coordination numbers by means of bulky groups. Single

5

crystal X-ray structures of $Fe[N(SiMe_3)_2]_3$[17] and $Cr(N^iPr_2)_3$[14] revealed that the MN_3 skeletons are trigonal planar and that ϕ, the dihedral angle between the NX_2 and MN_3 planes, is 49° and 71°, respectively. The other tricoordinate compounds of concern here can be assumed to possess a similar structure. Collectively, ESR data[14,18], magnetic data[19], and crystal field calculations[19] indicate that the ground state electronic configurations of the silylamides are

$$Ti[N(SiMe_3)_2]_3 \qquad {}^2A_1{}'$$

$$Cr[N(SiMe_3)_2]_3 \qquad {}^4A_2{}'$$

$$Fe[N(SiMe_3)_2]_3 \qquad {}^6A_1{}'$$
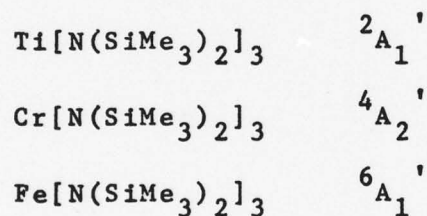
The dialykylamide, $Cr(N^iPr_2)_3$, has been shown[9] to have the same ground state electronic configuration as $Cr[N(SiMe_3)_2]_3$.

Curiously, despite the presence of unpaired electrons in the above silylamides no low energy ionizations attributable to metal-localized orbitals were detectable in the UPS[5].

The reason which was advanced for this phenomenon is that the metal MO's are stabilized significantly by the more electron-withdrawing $(Me_3Si)_2N$ groups, possibly causing them to be of comparable energies to the nitrogen lone pair MO's. Interestingly, $Cr(N^1Pr_2)_3$ does exhibit peaks at low IE which can be attributed to the ionization of metal-localized MO's (Figure 1a). The de-tailed assignment of the UPS of paramagnetic transition metal systems is, in general, a complicated matter[20,21] because of the large number of ionic states which can be generated upon photoionization (Table I). Arguing qualitatively, and on the basis of intensity considerations it is reasonable to assign peaks I_1 and I_2 to the production of the $^3A_2$ and ^3E ionic states via electron ejection from the Cr(3d) orbitals of a_2 and e symmetry, respectively (see below). In threefold symmetry the nitrogen "lone pair" MO's span the a_2 and e irreducible representations. However, as is clear from the nodal properties of such MO's (Figure 2) their relative energies are sensitive to the dihedral angle.[22] Obviously, at intermediate values of ϕ, a "cross-over" occurs, and, at some particular value of ϕ the a_2 and e MO's must be degenerate. Since the dihedral angle between the CrN_3 and NC_2 planes is 71° in $Cr(N^1Pr_2)_3$[14] the symmetry is nearer to $D_{3h}(1)$ than $D_{3h}(2)$. It is on this basis that we assign peaks I_3 and I_4 to the ionization of the a_2 and e nitrogen lone pair MO's respectively. The lack of resolution of peaks I_3 and I_4 could be due to two factors: (a) the possibility that both triplet and quintet A_2 and E states are observed in this region and (b) Jahn-Teller splitting of the E states. The

peak at 9.9 eV obviously represents the onset of ionization of the metal-nitrogen σ-bonding MO's (of symmetry a_1 and e); however, it is difficult to advance specific assignments.

The foregoing, qualitative interpretation of the UPS of $Cr(N^1Pr_2)_3$ is in good accord with the X_α SW calculation on the model compound $Cr(NH_2)_3$ (Tables II and III). Thus, the two highest occupied MO's (Table II) are primarily Cr(3d) in composition; the 6e MO is the degenerate $3d_{xz}$, d_{yz} set while the $4a_1$ is primarily $3d_z2$ (if the CrN_3 moiety lies in the xy plane). The $3a_2$ and 5e MO's are both mainly nitrogen lone pair; however, while the $3a_2$ is entirely localized on the nitrogens, the 5e has a small, but significant amount of density on chromium. This orbital is the π-bonding MO of the molecule and the orbital contour of one of the degenerate set is shown (in the xy plane) in Figure 3a. Since the nitrogen lone pairs are twisted out of the xy plane by only 19°, the best overlap is with the $d_x2_{-y}2$, d_{xy} set of orbitals on chromium. The wavefunction in Figure 3a shows nitrogen lone pair overlap with the Cr $3d_{xy}$ orbital. The next two MO's, 4e and $3a_1$, are the σ-bonding orbitals of the molecule. The contour of one of the degenerate 4e wavefunctions is shown in Figure 3b (xy plane), while the contour of the $3a_1$ MO (in the plane along the Cr-N σ bond, perpendicular to the xy plane) is illustrated in Figure 3c. The $3d_z2$ contribution to the σ-bonding is evidenced from the latter contour. The next four MO's, $2a_2$, 3e, 2e, and $2a_1$, are N-H σ-bonding, while the $1a_2$, 1e, and $1a_1$, are entirely Cr 3p and 3s in composition. It appears that the Cr $3d_x2_{-y}2$, d_{xy} set of e orbitals is involved in π-bonding (Figure 3a) as well as σ-bonding (Figure 3b) in the molecule.

8

It is of importance to note that the computed IE's (Table III) for the $4a_1$ and $6e$ metal-localized MO's are in the reverse order to the ground state eigenvalues (Table II), i.e. the HOMO ($6e$) is responsible for the second ionization. The breakdown of Koopmans' theorem in this instance is due to the relatively large relaxation energies which are associated with the photoionization of metal-rich orbitals: the higher the metal d orbital character, the more the MO will relax upon ionization. Thus, the $6e$ (87% metal) relaxes to a larger extent than the $4a_1$ (71% metal), causing the crossover in the observed UPS. This type of behavior is characteristic of the UPS of several transition metal compounds.[23]

The tetracoordinate dialkylamides of Cr and Mo are of interest because, while both are d^2 systems, $Cr(NEt_2)_4$ is paramagnetic yet $Mo(NMe_2)_4$ and $Mo(NEt_2)_4$ are diamagnetic. If the nitrogen geometry is taken to be trigonal planar and metal-nitrogen bond rotation is assumed to be slow on the UPS time scale, the maximum skeletal symmetry of a $M(NR_2)_4$ compound is D_{2d}. There are, in fact, two possible structures that possess this geometry: $D_{2d}(1)$ in which the C-N-C planes are perpendicular to the dihedral planes, and $D_{2d}(2)$ in which the C-N-C

planes are parallel to the dihedral planes. In T_d symmetry the metal nd orbitals split into the familiar e and t_2 sets; reduction of symmetry to $D_{2d}(1)$ or $D_{2d}(2)$ results in these orbitals transforming as b_1, a_1, b_2, and e as illustrated in Figure 4. In $D_{2d}(1)$ symmetry the nitrogen lone pair MO's, n_N, span the irreducible representations a_1, b_2, and e while in $D_{2d}(2)$ symmetry these transform as a_2, b_1, and e. Dative π bonding interactions are permitted between the nitrogen lone pair and metal nd MO's of the same symmetry as illustrated. Thus it is clear (Figure 4) that no interactions are possible with the b_1 ($d_{x^2-y^2}$) or $a_1(d_{z^2})$ metal and MO's in $D_{2d}(1)$ or $D_{2d}(2)$ symmetry, respectively. These orbitals are the HOMO's in low spin d^2 systems.

The crystal structure of $Mo(NMe_2)_4$ has been investigated recently[24] and the molecule has been found to adopt $D_{2d}(1)$ symmetry. The UPS of $Mo(NMe_2)_4$ (Figure 1b) is consistent with the ground state electronic configuration..$(a_1)^2(b_2)^2(e)^4(b_1)^2$. Thus, I_1 clearly corresponds to ionization of the b_1 metal localized MO, while peaks I_2, I_3, and I_4 can be assigned to electron ejection from the nitrogen lone pair MO's of symmetries e, b_2, and a_1, respectively on the basis of intensity consider-ations. The broad, intense peak at 10.7 eV represents ioniza-tion of the a_1, e, and b_2 molybdenum-nitrogen σ-bonding MO's of symmetries a_1, e, and b_2. The general correctness of this sequence of orbitals has been confirmed by Fenske-Hall calcula-tions on $Mo(NMe_2)_4$ which, in addition, revealed that the b_1 MO is 97% $4d_{x^2-y^2}$ in character, and that the e, b_2, and a_1 MO's

10

comprise 91, 94, and 71% ligand π character, respectively.[24]
The low value for I_1 (5.30 eV) is consistent with the Fenske-
Hall calculations on $Mo(NMe_2)_4$ which indicate that the b_1
MO is slightly antibonding. The UPS of $Mo(NEt_2)_4$ (Figure 1c)
is quite similar to that of $Mo(NMe_2)_4$ and can be assigned in
an analogous manner. As expected the energy required for pro-
duction of the $^2B_1$ state via electron ejection from the
$Mo(4d_{x^2-y^2})$ orbital is virtually identical in both compounds,
and slight inductive shifts are apparent in the IE's associated
with the nitrogen lone pair MO's. The somewhat more complex
appearance of the spectrum of $Mo(NEt_2)_4$ in the nitrogen lone pair
region could be due to (a) the actual symmetry of $Mo(NEt_2)_4$ being
lower than that of $Mo(NMe_2)_4$, or (b) an increased Jahn/Teller
splitting of the ^2E state in $Mo(NEt_2)_4$ compared to $Mo(NMe_2)_4$.

Interestingly, $Cr(NEt_2)_4$ (Figure 1d) is paramagnetic, although the
reasons for this are not clear at the present time. Probably
it is a reflection of the spin-pairing energies being in the
order Cr>Mo and the ligand field energies being in the order
Mo>Cr; alternatively, $Cr(NEt_2)_4$ could adopt the $D_{2d}(2)$ structure.
If so, the electronic configuration of the ground state would
be $(b_1)^2(e)^4(a_2)^2(a_1)^1(b_1)^1$ rather than $(a_1)^2(b_2)^2(e)^4(b_1)^1(a_1)^1$.
The ionic states emerging from the photoionization of both the
$D_{2d}(1)$ and $D_{2d}(2)$ ground state electronic configurations are
presented in Table I along with possible spectral assignments.
If one argues (probably in an oversimplified way) on the
basis of peak intensities the better fit is obtained with the
$D_{2d}(2)$ ground state structure. However, this conjecture, while

interesting, should be viewed cautiously. Clearly, the struc-
ture of $Cr(NEt_2)_4$ should be determined.

One of the intriguing aspects of the pentacoordinate amides
concerns the apparently close energies of the square pyramidal
and trigonal bipyramidal MN_5 geometries. Thus, it has been
demonstrated by X-ray crystallography that the NbN_5 moiety of
$Nb(NMe_2)_5$ approaches a square pyramidal structure[25], while
$Ta(NEt_2)_5$ has been found to adopt a trigonal bipyramidal geo-
metry for the TaN_5 skeleton.[26] The UPS of $Nb(NMe_2)_5$ and $Ta(NMe_2)_5$
are virtually identical (except for a small shift in the absolute
value of the IE's) and only the spectrum of the latter is
illustrated in Figure 1e. It thus appears that $Nb(NMe_2)_5$
and $Ta(NMe_2)_5$ are isostructural in the vapor phase. In a
square pyramidal (C_2) arrangement of MNC_2 moieties the five
peaks in the nitrogen lone pair region would correspond to the
ionization of two a and three b MO's. However, it is difficult
to be more specific without MO calculations. The lower IE's
are, therefore, listed without assignments in Table IV.

12

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Table I. Ionic States Resulting from Lower Energy Ionizations
of Open-Shell Metal Dialkylamides

$Cr(N^iPr_2)_3$

Ground State	Ion Configuration	Ionic State Produced	Experimental Ionization Energies[a]
$e^4 a_2^2 a_1^1 e^2 \; [^4A_2]$	$e^4 a_2^2 a_1^1 e^1$	^3E	6.53
	$e^4 a_2^2 e^2$	$^3A_2$	6.3
	$e^4 a_2^1 a_1^1 e^2$	$^3A_1$ $^5A_1$	7.38
	$e^3 a_2^2 a_1^1 e^2$	^3E ^5E	7.9
			9.9 (M–Nσ)

$Cr(NEt_2)4, \; D_{2d} (1)$

$a_1^2 b_2^2 e^4 b_1^1 a_1^1 \; [^3B_1]$	$a_1^2 b_2^2 e^4 b_1^1$	$^2B_1$	5.9
	$a_1^2 b_2^2 e^4 a_1^1$	$^2A_1$	6.3
	$a_1^2 b_2^2 e^3 b_1^1 a_1^1$	^2E ^4E	7.0
	$a_1^2 b_2^1 e^4 b_1^1 a_1^1$	$^2A_2$ $^4A_2$	7.2
	$a_1^1 b_2^2 e^4 b_1^1 a_1^1$	$^2B_1$ $^4B_1$	7.9
			10.0 (M–Nσ)

15

Table I. (cont'd.)

$$Cr(NEt_2)_4, \; D_{2d}(2)$$

$b_1{}^2 e^4 a_2{}^2 a_1{}^1 b_1{}^1 \; [^3B_1]$	$b_1{}^2 e^4 a_2{}^2 a_1{}^1$	$^2A_1$	5.9
	$b_1{}^2 e^4 a_2{}^2 b_1{}^1$	$^2B_1$	6.3
	$b_1{}^2 e^4 a_2{}^1 a_1{}^1 b_1{}^1$	$^2B_2$ $^4B_2$	7.0
	$b_1{}^2 e^3 a_2{}^2 a_1{}^1 b_1{}^1$	^2E ^4E	7.2
	$b_1{}^1 e^4 a_2{}^2 a_1{}^1 b_1{}^1$	$^2A_1$ $^4A_1$	7.9

^{a}All values in eV.

16

Table II. X_α SW "Ground State" Eignevalues and Charge Densities[a] for $Cr(NH_2)_3$

MO	ϵ[b]	Cr s	Cr s + p +	Cr d	Cr =total	N s	N + p	N =total	H s	OUTER[c] total	INT[d] total
7e	-1.00		0.03	0.63	0.66	0.01	0.06	0.07	0.00	0.02	0.11
6e	-3.41		0.00	0.87	0.87	0.00	0.01	0.01	0.00	0.00	0.10
$4a_1$	-3.53	0.07	0.00	0.64	0.71	0.00	0.00	0.00	0.00	0.02	0.27
$3a_2$	-4.60		0.00	0.00	0.00	0.00	0.23	0.23	0.00	0.00	0.31
5e	-5.72		0.04	0.10	0.14	0.00	0.18	0.18	0.00	0.02	0.30
4e	-8.76		0.06	0.26	0.32	0.01	0.18	0.19	0.01	0.02	0.03
$3a_1$	-9.23	0.14	0.01	0.13	0.27	0.01	0.19	0.20	0.02	0.00	0.01
$2a_2$	-12.88		0.01	0.01	0.01	0.01	0.19	0.19	0.07	0.00	0.00
3e	-12.93		0.00	0.02	0.02	0.00	0.19	0.19	0.07	0.01	0.00
2e	-20.69		0.02	0.01	0.03	0.22	0.01	0.23	0.04	0.00	0.04
$2a_1$	-20.81	0.02	0.01	0.01	0.03	0.23	0.01	0.24	0.04	0.00	0.01
$1a_2$	-46.28		1.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
1e	-46.38		0.99	0.00	0.99	0.00	0.00	0.00	0.00	0.00	0.01
$1a_1$	-73.51	1.00		0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00

[a] charge densities for atoms are the percentages of electron densities within the atomic spheres.

[b] eigenvalues in eV

[c] charge density outside outer sphere

[d] intersphere charge density inside outer sphere and not accounted for by atomic spheres; dashed line denotes a separation of HOMO and LUMO

Table III. Computed Ionization Energies for $Cr(NH_2)_3$ and
Experimental Ionization Energies for $Cr(N^iPr_2)_3$.

MO	Computed IE[a]	Experimental IE[a]
$4a_1$	6.76	6.3
$6e$	7.01	6.53
$3a_2$	7.52	7.38
$5e$	8.57	7.9
$4e$ } $3a_1$		9.9

[a]All values in eV.

18

Table IV. Ionization Energy Data[a] for $M(NR_2)_4$ and $M(NR_2)_5$ Compounds

<u>$M(NR_2)_4$</u>

Ionic State	$Mo(NMe_2)_4$	$Mo(NEt_2)_4$
$^2B_1(d_{x^2-y^2})$	5.30	5.3
$^2E(n_N)$	7.34	7.0[b], 7.3[b]
$^2B_2(n_N)$	7.70	7.56
$^2A_1(n_N)$	9.01	8.7
M-N ionizations	10.7	

<u>$M(NR_2)_5$</u>

	$Nb(NMe_2)_5$	$Ta(NMe_2)_5$
n_N	6.77	6.89
	6.9	7.1
	7.63	7.78
	8.02	8.15
	8.21	8.35
M-N ionizations	9.7, 10.2	9.7, 10.4

[a] All values in eV

[b] Splitting due to the Jahn-Teller effect. See text.

19

Figure Captions

Figure 1.   He(I) UPS of :   (a) $Cr(N^iPr_2)_3$; (b) $Mo(NMe_2)_4$;
            (c) $Mo(NEt_2)_4$; (d) $Cr(NEt_2)_4$; and (e) $Ta(NMe_2)_5$.

Figure 2.   Horizontal ($D_{3h}(1)$, $\phi=90°$) and vertical ($D_{3h}(2)$,
            $\phi=90°$) arrangements of $N(2p)$ AO's in threefold symmetry.

Figure 3. X_α SW contour plots for the following MO's of
            $Cr(NH_2)_3$:   (a) one of the two degenerate 5e wavefunctions
            (CrN_3 plane); (b) one of the two degenerate 4e
            wavefunctions (CrN_3 plane); (c) the $3a_1$ wavefunction
            (perpendicular to CrN_3 plane, along CrN bond).   Contour
            values are: $1=\pm0.20$; $2=\pm0.10$; $3=\pm0.05$; $4=\pm0.02$.

Figure 4.   A qualitative MO scheme for $M(NR_2)_4$ complexes
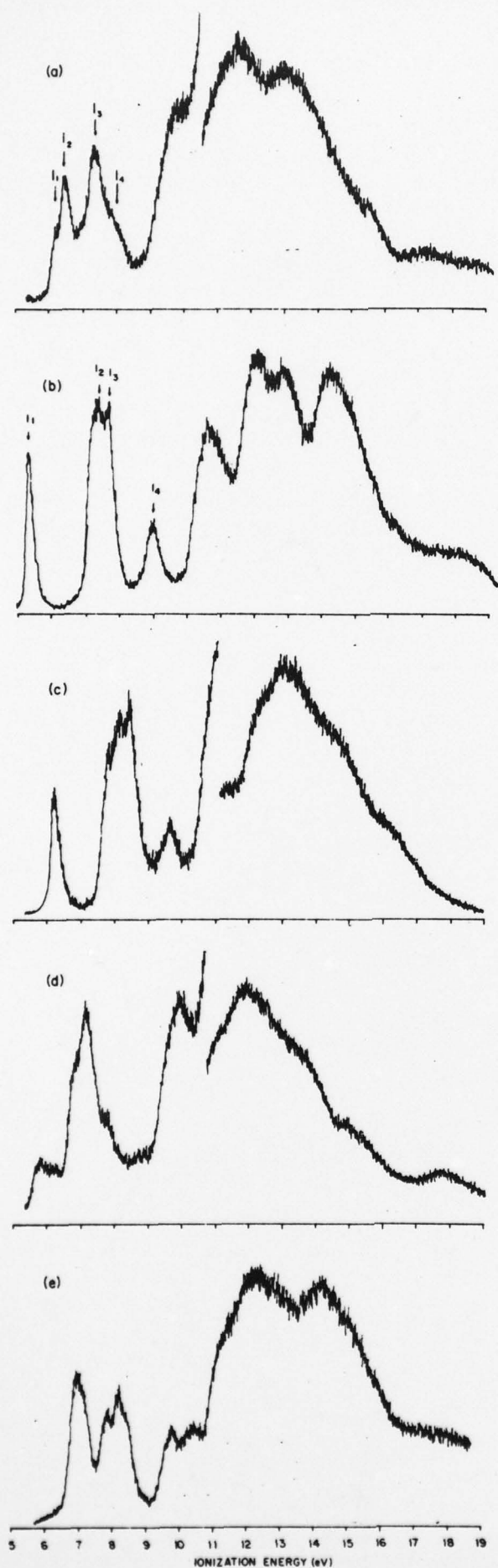   in two different D_{2d} configurations (see text).

20

Figure 1
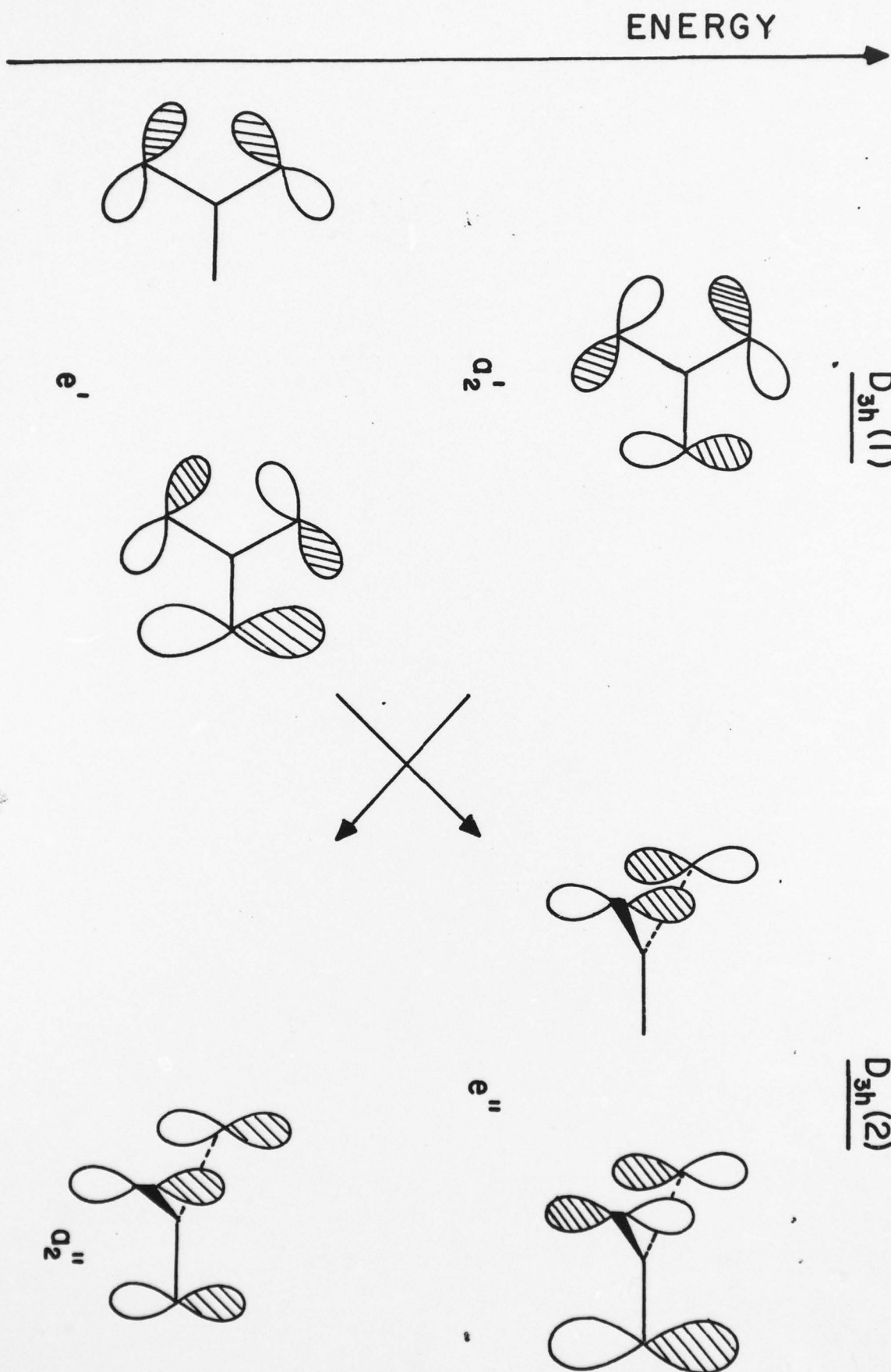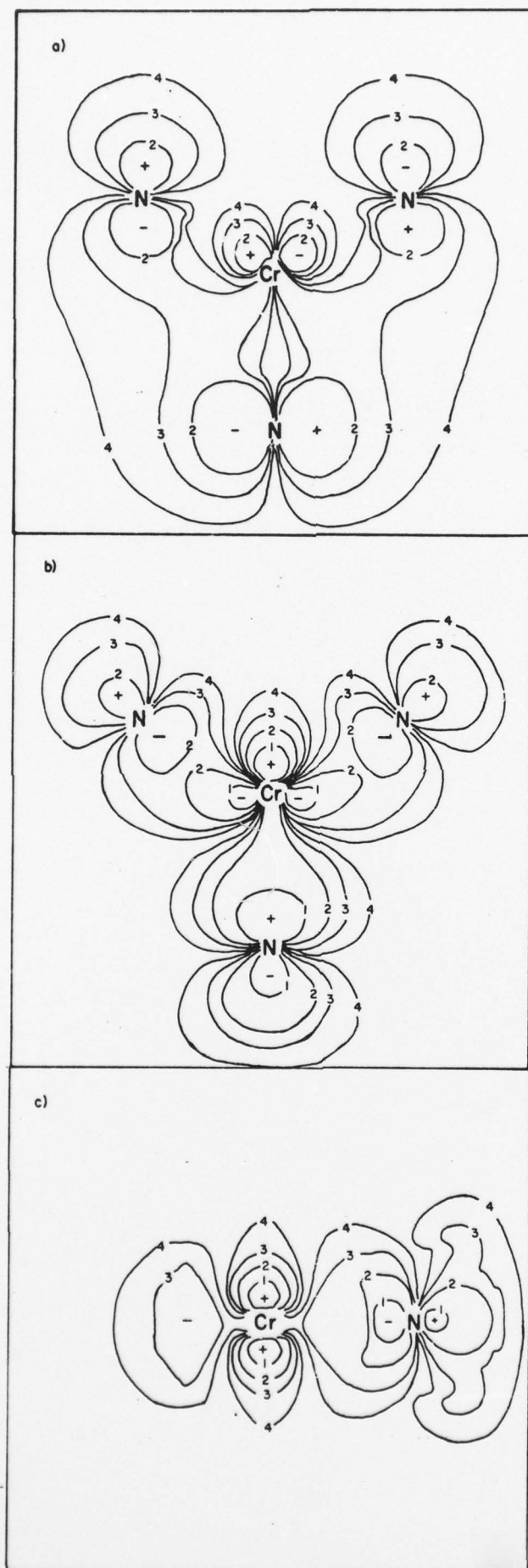
IONIZATION ENERGY (eV)

ENERGY

$\dfrac{D_{3h}(1)}{}$

a'_2

e'

$\dfrac{D_{3h}(2)}{}$

e''

a''_2

Figure 2

a)

b)

c)

Figure 3

Figure 4

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